

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of: Imam et al.  
Serial No.: 08/845,897  
Filed: 08/28/1997  
For: POROUS METAL/ORGANIC POLYMERIC COMPOSITES  
Examiner: Vo, Hai  
Art Group Unit: 1771

DECLARATION UNDER 37 C.F.R. § 1.131 OF M. ASHRAF IMAM  
AND TEDDY M. KELLER

We, M. Ashraf Imam and Teddy M. Keller, hereby declare that:

1. We are co-inventors with Bhakta B. Rath (inventors) of the invention claimed in the above-identified patent application (application).
2. Attached is a copy an invention disclosure prepared by the inventors, which formed the basis of the application.
3. The Execution of Disclosure shows the signatures of M. Ashraf Imam and Teddy M. Keller, which was in fact, to the best of our recollections, signed on 07/30/1996 as shown. The contents of the disclosure were complete at the time that it was signed.
4. All work described in the disclosure was performed by the inventors or at their direction, no later than 07/30/1996 in a NAFTA or WTO member country.
5. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

7/12/2006

Date

M. Ashraf Imam

M. Ashraf Imam

7/12/06

Date

Teddy M. Keller

Teddy M. Keller

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DECLARATION UNDER 37 C.F.R. § 1.131 OF BHAKTA B. RATH

I, Bhakta B. Rath, hereby declare that:

1. I am a co-inventor with M. Ashraf Imam and Teddy M. Keller (inventors) of the invention claimed in the above-identified patent application (application).
2. Attached is a copy an invention disclosure prepared by the inventors, which formed the basis of the application.
3. All work described in the disclosure was performed by the inventors or at their direction, no later than 07/30/1996 in a NAFTA or WTO member country.
4. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

7/12/06  
Date

Bhakta B. Rath  
Bhakta B. Rath

## PURPOSE:

This invention relates to the preparation of novel metal/organic polymer composites from metallic foams and polymeric resins. In the Navy, for ships and submarines, it is highly desirable that the noise generated by machinery during normal operations be absorbed within the platform in order to reduce the detectability and identifiability of these platforms. The two primary approaches to this goal are the use of soft coupling components (e.g. bushings, pads) to isolate machinery and the incorporation of structural materials which highly attenuate acoustic vibrations. Neither of these approaches is currently fully satisfactory. While the coupling components add weight, can require maintenance and may not be consistent with required design and performance features, the currently available damping materials do not exhibit adequate acoustic behavior over broad ranges of temperature, do not have the required strain amplitude and frequency or do not have the desired strength and environmental resistance. In addition to solving these problems, the vibrational damping exhibited by the composites of this invention can also lead to a reduction of the wear rate (e.g. of ball bearings) in rotating machinery and improve the accuracy of laser or particle beam weapon systems.

## BACKGROUND:

Significant advances have been made to increase the strength and stiffness of lightweight materials. Examples of these developments include the superior density-normalized strength and stiffness of Al-Li, hard dispersion strengthened aluminum and titanium, aluminides, and whisker or fiber reinforced aluminum and magnesium. Although the designers of structures have welcomed these increases in mechanical properties, there is a persistent demand that these materials should also exhibit much higher intrinsic capacity to damp. Capabilities developed at NRL place us in the unique position to introduce a new breed of lightweight, isotropic composite materials with high damping capacity and outstanding mechanical properties.

## DESCRIPTION AND OPERATION:

Metal/organic polymer composites have been made by impregnating porous metals/alloys having isotropic properties with elastomers (silicon rubber), acrylic, phenolic, epoxies, and with high temperature, flame resistant phthalonitrile-based polymer developed at the Naval Research Laboratory. Any porous metal with various percent density can be used as part of this invention. The specific composites studied were made of porous aluminum (Al) alloy, titanium, and steel. As an example, phthalonitrile/Al composites were made from high temperature phthalonitrile resin and porous Al (6-8% density, 40 ppi). Phthalonitrile monomer [4,4'-bis(3,4-dicyanophenoxy)-biphenyl] was first melted at 250 °C and degassed for about an hour to remove trace amounts of volatiles trapped in the monomer. The monomer was then converted to a prepolymer by adding 1.8 % by weight of a curing additive [1,3-bis(3-aminophenoxy)benzene] and stirring for 15 min. The prepolymer melt was poured into steel molds containing the porous Al sample and degassed for an additional half an hour at 250 °C. Small weights on a teflon film were placed on top of the Al block to keep it submerged in the resin. Composite samples were then cured in an air circulating oven for varying times of 2, 9 and 18h at 280 °C. Samples were then postcured by heating in sequence at 325 °C for 4h, at 350 °C for 4h, and at 375 °C for 4h under an inert atmosphere (argon). The resulting light weight composite exhibited high damping capacity, outstanding fire resistance and high isotropic mechanical properties (see Figures 1 and 2). Figures 1 and 2 show the damping profile of phthalonitrile/Al composite fabricated under various curing conditions and the stress-strain behavior, respectively. Vacsosil is the current state-of-the-art damping material. Figure 3 shows the  $\tan \delta$  for

several materials including vacrosil and the phthalonitrile/Al composite over frequency ranges of 0.1 to 10Hz. The acoustic behavior exhibited by the phthalonitrile/Al composite is far superior to that of current state-of-the-art (SOA) damping materials.

Phthalonitrile Prepolymer + Al Foam → Phthalonitrile-Aluminum Composite  
Epoxy Resin + Al Foam → Epoxy-Aluminum Composite  
Acrylic Resin + Al Foam → Acrylic-Aluminum Composite  
Silicon Rubber + Al Foam → Silicon Rubber-Aluminum Composite  
Phenolic Resin + Al Foam → Phenolic-Aluminum Composite  
Phthalonitrile Prepolymer + Ti Foam → Phthalonitrile-Titanium Composite  
Phthalonitrile Prepolymer + Steel Foam → Phthalonitrile-Steel Composite

#### ADVANTAGES AND NEW FEATURES:

Materials with high stiffness and strength are required in many important applications. Moreover, metals and alloys which possess a large inherent damping capacity have been extensively sought for many domestic and military applications. Some specific applications include gears and gear webs, pump castings, engine parts, and propellers. Components fabricated from the metal foam/polymer composites of this invention will not only be affordable but will also provide high damping capacity, which will affect the signatures, be lightweight, and exhibit outstanding fire resistance and good mechanical properties. It is noted that this class of composite materials has the following advantages: the metal component will provide lightweight, isotropic mechanical strength and the polymeric phase will produce the attenuation attributed to the softening effect above the glass transition temperature or by relative motion or deformation at the interface between the two phases. It is important to emphasize that the choice of materials is such that the interim results would be of extreme technological interest to designers of near-future weapons and weapon platforms and in the design of structural component for both ship and aerospace applications. Besides the enhancement in performance, the usage of such composite materials would be expected to affect the radar signatures of ships, aircraft, and missiles fabricated from these novel composite materials. Any metallic foam and processable polymeric resins can be used in the fabrication of composite components. Novel composite components can be easily fabricated by resin transfer molding (RTM). Numerous metal foams, e. g., Al, Ti, Steel, Ni, Cu and carbon foam can be used with various densities, which will affect the overall performance of the resulting composite. For domestic applications, metal foam/organic polymeric composites could be very useful in the design of energy efficient cars. Moreover, car components fabricated from the composite materials of this invention would be expected to exhibit improved impact resistance relative to currently used metals. The metal foam/phthalonitrile composites would also be expected to show outstanding flammability properties. Due to the superior flame resistance exhibited by the phthalonitrile polymer, improvements in the flame resistance of phthalonitrile/Al composite relative to Al metal at elevated temperature would be expected.

The novel metal foam/ organic polymeric composites of this invention could represent a major technological breakthrough in the design of composite components for applications under extreme environmental conditions. These advanced materials could potentially be used as high

temperature, high performance structural materials for extraterrestrial vehicles such as the national aerospace plane (NASP), the next generation space shuttle, reusable launch vehicles/boosters, high performance heat engines, gas turbine engines, heat exchangers, and electronic applications.

#### ALTERNATIVES:

Research on metal foam/organic polymer composites started around 1986 at NRL. Many composites have been fabricated and evaluated for their damping characteristics. These novel composites exhibit other unique physical characteristics such as lightweight and good mechanical properties for structural applications. The novel metal foam/phthalonitrile composites of this invention are the first described flame resistant composites fabricated from metal foam and polymeric materials for applications under extreme environmental conditions and exhibit superior acoustic behavior relative to any other structural material. The phthalonitrile-based composites, which exhibit superb processability, can be readily fabricated through the cyano groups of the phthalonitrile units yielding high temperature thermosetting metal foam/organic polymeric composites that exhibit outstanding long term thermo-oxidative properties.

#### CONTRIBUTIONS BY INVENTORS:

This invention was a collaboration between M.A. Imam of the Materials Science and Technology Division, Code 6323, Teddy M. Keller of the Chemistry Division, Code 6120, and Bhakta B. Rath, Code 6000.

#### EXECUTION OF DISCLOSURE

Inventors

Date

Ullah B. Imam

7/30/96

Teddy M. Keller

7/30/96

Witness

Disclosed and understood by me on

Date

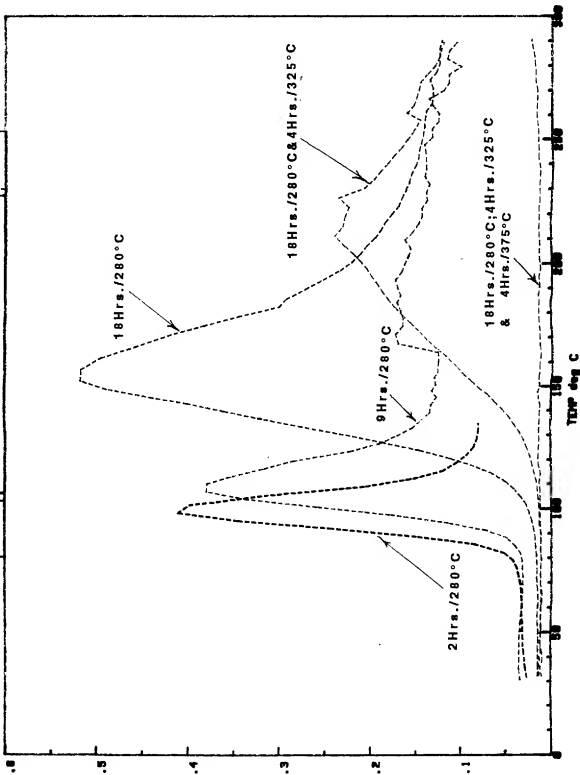
Robert F. Sradley

7/30/96

Chad D. Smith

7/30/96

Phth~~er~~thal~~ic~~ acid / Carbonyl Chloride  
 18Hrs./280°C & 4Hrs./325°C

Tan  $\delta$ 

PD  
DMTA

--- 1 Hz

B.I. & I.B.  
 STRAIN -4  
 2 deg/min  
 -LOAD 2.010  
 DUAL CONT  
 4.1000000000000000  
 CLAMP 0-1  
 FILE PRO  
 BY ISB  
 ON 22/05/84

